An ab initio and dynamics study of the photodissociation of nitric acid HNO3

Nonella, M ; Suter, H U ; Huber, J R

Abstract: We investigated the photodissociation of HNO3 within the first (300 nm) and the third (200 nm) absorption band. The relevant S1 and S3 potential energy surfaces were calculated by taking into account the N-O single bond and N=O “double” bond distances. The striking feature of the dynamical analysis is a bifurcation of the wave packet on the S3 surface which explains the branching into the two reaction pathways with the products OH+NO2 and O+HONO found in experiments. Dissociation on the S1 surface is predicted to proceed along a single channel leading to OH+NO2, both in their electronic ground states. Corresponding author:

DOI: https://doi.org/10.1016/j.cplett.2010.01.005

Corrected Version

An *ab Initio* and Dynamics Study of the Photodissociation of Nitric Acid HNO_3

M. Nonella, H.U. Suter and J. Robert Huber

Physikalisch-Chemisches Institut der Universität Zürich
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Abstract

We investigated the photodissociation of HNO_3 within the first (300 nm) and the third (200 nm) absorption band. The relevant S_1 and S_3 potential energy surfaces were calculated by taking into account the N-O single bond and N=O "double" bond distances. The striking feature of the dynamical analysis is a bifurcation of the wave packet on the S_3 surface which explains the branching into the two reaction pathways with the products $OH+NO_2$ and O+HONO found in experiments. Dissociation on the S_1 surface is predicted to proceed along a single channel leading to $OH+NO_2$, both in their electronic ground states.

Corresponding author:
J. Robert Huber
Physikalisch-Chemisches Institut
Universität Zürich
Winterthurerstrasse 190
CH-8057 Zürich, Switzerland
e-mail: jrhuber@pci.uzh.ch
FAX: 0041-44635 6838

ms. Microsoft Word

Introduction

The photochemical decay of nitric acid HNO_3 in the gas phase has been well investigated motivated mainly by the importance of this molecule for atmospheric chemistry [1-2]. Just recently the first global distributions of nitric acid in the troposphere and the stratosphere have been reported employing infrared satellite measurements [3]. With respect to solar photolysis, which is probably the most efficient removal process of HNO_3 in the atmosphere, the absorption spectrum [4] of HNO_3 can be considered in terms of two intervals. The first around 200 nm is relevant for photolysis in the higher stratosphere above 25 km and is thus unfiltered by O_3, O_2 and N_2 , and the second one around 300 nm for altitudes below 20 km. The spectrum starts with a very weak and broad absorption band which rises to a maximum at 260 nm followed by a strong and structureless band centred near 190 nm. These bands were assigned to the $S_0 \rightarrow S_1(n\pi^*)$ and $S_0 \rightarrow S_3(\pi\pi^*)$ transitions, respectively, both strongly localized on the NO_2 group of the molecule [5]. Irradiation into the weak $n\pi^*$-absorption band at 260 nm was found to yield the photoproducts OH + NO_2 (1), both in their electronic ground states, with a quantum yield Ø near unity [6,7]. If the excitation wavelength is decreased to the region between 220 and 190 nm an additional decay channel becomes active giving rise to the products O + HONO. The various photodissociation pathways emerging from this excitation process are summarised in the following scheme [2]:

$$HNO_3 + h\nu \rightarrow OH(X) + NO_2\,(X\,^2A_1) \qquad \Delta H° = 200\ kJ/mol \quad (1)$$

$$\rightarrow OH(X) + NO_2\,(1\,^2B_2) \qquad \Delta H° = 315\ kJ/mol \quad (2)$$

$$\rightarrow O\,(^1D) + HONO(\tilde{X}\,^1A') \qquad \Delta H° = 490\ kJ/mol \quad (3)$$

$$\rightarrow O\,(^3P) + HONO\,(\tilde{a}\,^3A'') \qquad \Delta H° = 550\ kJ/mol \quad (4)$$

$$\rightarrow O\,(^3P) + HONO\,(\tilde{X}\ ^1A') \qquad \Delta H° = 300\ kJ/mol \quad (5)$$

Photolysis at 193 nm is dominated by the formation of O + HONO [8,9] with a total quantum yield of 0.67 (Ø = 0.54 and 0.13 for channel (3) and (4), respectively [9] and Ø = 0.33 for (1) and (2)). This clear preference of the breaking of the strong -N=O bond (~ 500 kJ/mol) over that of the much weaker -N-O bond (~200 kJ/mol) at higher excitation energy is somewhat surprising and let to speculations about the mechanistic features of this branching process [2]. Mainly for this reason we extended the previous theoretical work of Bai and Segal [5] and investigated the photodissociation of HNO_3 using ab initio and dynamics calculations. For the relevant $S_1(1^1A")$ and the $S_3(2^1A')$ states we constructed two-dimensional potential energy surfaces PESs along the two dissociation coordinates –N=O and –N-O, and explored the initial wave packet dynamics to explore the dissociation paths.

Methods of Calculations

The study is based on two-dimensional *ab initio* potential energy surfaces of the first and third electronically excited states S_1 and S_3 of HNO_3. Guided by the experimental findings we choose the coordinates r(N-O) responsible for the dissociation of channels (1) and (2) and the coordinate r(N=O) in trans position which is expected to be involved in the bond breaking of channels (3-5).

The calculations of the PESs were carried out with the COLUMBUS program package [10] at the CASSCF level of theory in conjunction with the DALTON suite programs [11] using an optimized planar ground state geometry of HNO_3 : H- O 95.4 nm, N-OH 140.6 nm, N-O_c 121.6 nm, N-O_t 120.8 nm, H-O-N 103°, HO-N-O_c 117°, HO-N-O_t 113°. These parameters are in excellent agreement with the geometry determined by microwave spectroscopy [12]. The ground state consists of 13 a' and 3 a" occupied molecular orbitals. The S_1 PES and S_3 PES were calculated with the following basis set [13]: 10s6p1d contracted to 6s3p1d used for oxygen and nitrogen, and 5s1p contracted to3s1p for hydrogen.

This set leads to 140 basis functions which were contracted to 86 functions. The exponents of the polarization functions were 1.2 for oxygen, 1.0 for nitrogen, and 0.8 for hydrogen. The active space for the CASSCF calculation involved the orbitals 11a' to 16 a' and 2a" to 5a" . This active space yielded 9772 configurations for symmetry a' (S_3 state) and 9632 configurations for symmetry a" (S_1 state).

The wave packet calculation was performed on a 64 x 64 grid obtained by a spline interpolation of the computed *ab initio* points. The initial wave packet was taken to be identical to the wave function of the vibrational ground state of S_0 as derived from the harmonic approximation to the S_0 PES. Thus the transition dipole is coordinate independent. The ground state frequencies corresponded to 694.4 (O-N) and 1456.6 cm^{-1} (N=O) with the Franck-Condon (FC) point at r_0(O-N) = 2.65 a.u. and r_0(N=O) = 2.29 a.u. Applying the split-operator technique of Feit and Fleck [14,15] the wave packet $\Phi(r_1, r_2, t)$ was propagated in time steps of 0.1 fs.

The vertical excitation energies and their oscillator strengths for the lowest four electronic transitions in HNO_3 were calculated by two different methods. Using the same basis set as in the PES calculations (see above) we applied a second-order polarization propagator approximation, SOPPA (CCSD) [16,17] and the CASSCF N-electron valence state perturbation theory NEVPT2 [18,19].

Results

In its electronic ground state nitric acid is a planar molecule with C_s symmetry. The small deviation from C_{2v} symmetry is due to the position of the H atoms which causes the two NO bonds to be slightly inequivalent (cf. insert in Fig. 1). In electronically excited states this geometry can relax to a pyramidal form where the NO_2 group is bent down out of plane and the H atom is rotated by 90° about the single N-O bond [2,5]. For the S_1 state the energy difference of the two optimized geometries was found to be 15.6 kcal/mol with the pyramidal

structure being the lower. Our calculations of the PESs are based on the planar ground state geometry since the fast dissociation, indicated by a totally structureless absorption continuum and the measured S_3 lifetime of < 80 fs [20], was assumed to prevent a substantial geometrical relaxation prior to bond breaking.

The vertical excitation energies to the S_1, S_2 and S_3 electronic states are listed in Table1 together with the oscillator strengths or absorption cross sections. The first two transitions, which are out of plane (z) and in C_{2v} symmetry dipole forbidden, carry a very small oscillator strength. The strong $S_0 \square S_3$ transition lies in the molecular plane and is directed parallel to the line connecting the two terminal O atoms (y) (see insert Fig.1).

The S_1 and S_3 potential energy surfaces of HNO_3 are shown as contour plots in Fig. 1. They were calculated with variations of the N-O and the N=O bond lengths while keeping all other coordinates fixed at their ground state values. The S_1 PES reached by an $S_0 \rightarrow S_1(1^1A")$ transition with an energy calculated to be 3.68 eV (SOPPA) shows a distinct exit channel along the N-O single bond roughly parallel to the ground state N=O bond distance. Around the FC point the potential is almost flat up to an N-O bond length of ≈ 3.2 a.u. where a steep decline is observed. A continuous decline of the potential finally leads to the creation of the products HNO and NO_2. This is further illustrated by a cut through the S_1 PES parallel to the N-O distance at the FC point as depicted in Fig. 2c. We also carried out a cut through the S_1 potential at a fixed N-O distance of 4.8 a.u. parallel to the N=O distance to obtain the approximate Morse potential of free NO_2. The dissociation energy thus obtained is 69.8 kcal/mol in close agreement with 71.8 kcal/mol reported for the free NO_2 molecule [21]. The result indicates that the calculated S_1 PES represents the potential of dissociation channel (1) with the products $OH(X) + NO_2(X\ ^2A_1)$.

The upper part of Fig. 1 depicts the S_3 PES which is accessible by 193 nm excitation. The vertical $S_0 \rightarrow S_3(2^1A')$ transition energy is calculated to be at 5.81 eV (213 nm) (see Table 1, SOPPA). In contrast to the S_1 PES this contour plot is characterized by two exit channels one leading to the bond-breaking of the N-O single bond, the other to a scission of the N=O "double" bond. From the FC point the potential of both channels shows a steep decline towards the exit. This behavior is demonstrated in Figs. 2a and 2b by cuts through the PES at the FC point along the respective dissociation coordinate. Furthermore, the position of the FC point where the wave packet is initially created, let us surmise that after creation, the moving wave packet is subject to a bifurcation. This expectation was justified as is demonstrated by the wave packet evolution in Fig. 3. The four snap shots show the wave packet $\Phi(r_1,r_2,t)$ at its creation at the FC point, after 7fs, 13 fs, and 15 fs. During the movement it splits up into two parts; about 60% of the WP enters the steep exit channel to form O + HONO, and about 40% of it moves into the other sharply declining exit channel to form OH + NO_2. For the latter channel the calculation further revealed the nature of the NO_2 state. Based on the molecular orbital picture of the NO_2 moiety taken at an N-O distance of 4.8 a.u. in the dissociating HNO_3 molecule, the departing NO_2 is in the excited B_2 state. Thus the dominant pathway of this channel [8,9] leads to OH(X) + $NO_2(1^2B_2)$ corroborating the previous analysis of Myers et al. [9].

Discussion and Conclusion

The absorption spectrum of HNO_3 between 325 and 185 nm lacks any vibronic structure [22,23]. Within this range three electronic transitions can be distinguished with 0-0 transitions estimated to be at ≈ 320, 260 and 210 nm. The result of the *ab initio* SCF calculations of the vertical excitation energies and oscillator strengths given in Table 1 support the assignment of these three lowest electronic transitions. In particular the SOPPA (CCSD) method furnishes spectral parameters for HNO_3 which are in good agreement with experiment

including the directions of the transition moments provided experimentally by vector correlation measurements in photodissociation [8,9,24]. Most of the reported experiments were carried out with irradiations at 280 nm (about 13 kcal/mol above the S_1 0-0 transition) and at 193 nm (about 12 kcal/mol above the S_3 0-0 transition).

According to the topography of Fig. 1 photon excitation to the S_1 PES produces exclusively the fragments OH + NO_2 both in their electronic ground state (1). By probing scalar and vector properties of the OH(X) fragment after excitation at 280 nm Simons et al. [24,25] suggested a tendency of the excited HNO_3 molecules to deform from the planar to a pyramidal form prior to dissociation. It is conceivable that such a geometrical relaxation which brings the pyramidal form about 15 kcal/mol below the planar form, could further enforce a fast dissociation along this channel. A fast dissociation is clearly indicated by the structurless $S_0 \square S_1$ absorption spectrum and the magnitude of the fragment anisotropy parameter. Although the PES is relatively flat around the FC point, a steep decline into the exit channel starts at a N-O elongation of about 3 a.u. (see Fig. 2c) driving the molecule into dissociation.

Excitation into the S_3 PES at 193 nm [2,8,9,26] results in a more complex picture of photodissociation characterized by two chemically different reactions ,one leading to OH + NO_2 (1-2) the other one to O + HONO products(3-5). Following preparation within the FC area (Fig. 1) two steep potential energy descents along the N-O and N=O coordinates, clearly manifested in Figs. 2a and 2b, can drive the excited molecule into dissociation. The four snap shots of the wave packet dynamics in Fig. 3 demonstrate these dissociation processes to be very fast. After 7fs following preparation the wave packet starts to broaden and after about 13 fs a separation into two parts becomes apparent with the greater portion of about 60% moving into the O + HONO channel. Such a branching ratio of roughly 60:40 conforms well to the measured quantum yields of 0.67 and 0.33 for the O + HONO and the OH + NO_2 channels, respectively [9]. The

branching into the two direct dissociation channels by a bifurcation occurs almost immediately after the excitation process on the S_3 PES. According to this result the involvement of two different and repulsive electronic surfaces connected by internal conversion is not necessary to explain the origin of this branching [2]; the initial step takes place on a single PES. Furthermore the experimental findings show that the final products are not exclusively in the electronic ground state, or where symmetry arguments indicate, in the excited state. For reaction (2) and (4) an additional branching may be involved at larger N-O and N=O bond distances on the S_3 PES. The high energetic S_3 state as well as the lower S_1 state are subject to crossings and avoided crossings by other PESs which make further branching feasible.

In conclusion, on the basis of *ab initio* and dynamics calculations of the S_1 and S_3 PESs of HNO_3, which are the origins of different photodissociation products, it is predicted that the two different chemical pathways of photodissociation to NO_2 + OH on the one hand and to O + HONO on the other can be explained by a wave packet bifurcation [27] occurring shortly after the excitation process on the S_3 PES. With excitation into the S_1 state the calculations predict only one open dissociation channel with the products NO_2 + OH in their electronic ground states. These results also apply to a great extent to methyl nitrate CH_3ONO_2, the methyl-substituted nitric acid. Its photodissociation is characterized by the same branching with the products CH_3O + NO_2 and CH_3ONO + O [28].

References

[1] B.J. Finlayson-Pitts, J.N. Pitts Jr., Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications, Academic Press, New York 2000.

[2] J.R. Huber, ChemPhysChem, 5 (2004) 1663.

[3] C. Wespes, D. Hurtmans, C. Clerbaux, M.L. Santee, R.V. Martin, P.F. Coheur, Atmos. Chem. Phys. 9 (2009) 7949.

[4] J.B. Burkholder, R.K. Talukdar, A.R. Ravishankara, S. Solomon, J. Geophys. Res. D98 (1993) 22937.

[5] Y.Y. Bai, G.A. Segal, J. Chem. Phys. 92 (1990) 7479.

[6] G.S. Jolly, D.L. Singleton, D.J. McKenney, G. Paraskevopoulos, J. Chem. Phys. 84 (1986) 6662.

[7] M.J. Krisch, M.C. Reid, L.R. McCunn, L.J. Butler, J. Shu, Chem. Phys. Lett. 397 (2004) 21.

[8] P. Felder, X. Yang, J.R. Huber Chem. Phys. Lett. 215 (1993) 221.

[9] T.L. Myers, N.R. Forde, B. Hu, D.C. Kitchen, L.J. Butler, J. Chem. Phys. 107 (1997) 5361.

[10] H. Lischka, R. Shepard, , I. Shavitt, R.M. Pitzer, M. Dallos, Th. Müller, P.G. Szalay, F.B. Brown, R. Ahlrichs, H. J. Böhm, A. Chang, D.C. Comeau, R. Gdanitz, H. Dachsel, C. Ehrhardt, M. Ernzerhof, P. Höchtl, S. Irle, G. Kedziora, T. Kovar, V. Parasuk, M.J.M. Pepper, P. Scharf, H. Schiffer, M. Schindler, M. Schüler, M. Seth, E.A. Stahlberg, J.-G. Zhao, S. Yabushita, Z. Zhang, M. Barbatti, S. Matsika, M. Schuurmann, D. R. Yarkony, S. R. Brozell, E.V. Beck and J.-P. Blaudeau, COLUMBUS, an ab initio electronic structure program, release 5.9.1.(2006).

[11] Dalton, a molecular electronic structure program, Release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html

[12] A.P. Cox and J.M. Riveros, J. Chem. Phys. 42(1965) 3106.

[13] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829

[14] M.D. Feit and J.A. Fleck, J. Chem. Phys. 80 (1984) 2578.

[15] R. Kosloff, J. Phys. Chem. 92(8) (1988) 2087.

[16] E.S. Nielsen, P. Jorgensen, J. Oddershede, J. Chem. Phys. 73 (1980) 6238.

[17] S.P.A. Sauer, J. Phys. B (1997) 3773.

[18] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, J. Chem. Phys. 114 (2001) 10252.

[19] C. Angeli, R. Cimiraglia, J.-P. Malrieu, J. Chem. Phys. 117 (2002) 9138.

[20] F. Assenmacher, M. Gutmann, F. Noack, V. Stert, W. Radloff, Appl. Phys. B 71 (2000) 385.

[21] U. Robra, H. Zacharias and K.H. Welge Z. Physik D 16 (1990) 175.

[22] H.S. Johnston and R. Graham, J. Phys. Chem. 77 (1973) 62.

[23] F. Biaume, J. Photochem. 2 (1973-74) 139.

[24] J. August, M. Brouard and J.P. Simons, J. Chem. Soc. Faraday Trans. 84 (1988) 587.

[25] M. Brouard, S. Duxon, P.A. Enriquez and J.P. Simons, J. Chem. Soc. Faraday Trans. 89 (1993) 1435.

[26] Q. Li, R.T. Carter, J.R. Huber, Chem. Phys. Lett. 257 (1996) 481.

[27] H.U. Suter, J.R. Huber, M.v. Dirke, A. Untch, R. Schinke, J. Chem. Phys. 96 (1992) 6727.

[28] X. Yang, P. Felder, J. R. Huber, J. Phys. Chem. 97 (1993) 10903.

Figure Captions

Figure 1. Contour plots of the calculated potential energy surfaces of the S_1 and the S_3 state as a function of the N=O "double" bond and the N-O single bond of HNO_3. The energy spacing is 0.021 a.u. (0.57 eV). The circle marks the equilibrium geometry (FC point) as determined for the electronic ground state. The FC points taken as reference energy for the contours are at -279.511 a.u. (S_1) and -279.417 a.u. (S_3).

Figure 2. Cuts through the S_3 (a,b) and the S_1 (c) potential energy surfaces at the FC point and along the dissociation coordinates N=O and N-O, respectively.

Figure 3. Snapshots of the evolving wave packet $\Phi(r_1,r_2,t)$ on the S_3 potential energy surfaces. Plotted is $|\Phi(r_1,r_2,t)|$; for each figure the wave packet is set to one.

Table 1: Vertical excitation energies [eV] and oscillator strengths.

	SOPPA (CCSD)	CASSCF/ NEVPT2	Lit. [5]	Exp. [22,23]
$S_0(A')\rightarrow S_1(A'')$ (z)	3.68 (3.93×10^{-6})	4.78	4.59 (2×10^{-6})	3.9 ($\sim 3 \times 10^{-21}$) [a]
$S_0(A')\rightarrow S_2(A'')$ (z)	4.76 (2.26×10^{-4})	5.11	5.59 (4×10^{-5})	4.6 (1.9×10^{-20}) [a]
$S_0(A')\rightarrow S_3(A')$ (y)	5.81 (0.19) [b]	7.07	6.88 (0.3)	5.9 (1.6×10^{17}) [a]
$S_0(A')\rightarrow S_4(A')$ (x)	6.34 (0.036) [b]	7.27		

a) Absorption cross section [cm^2] taken at the maximum of the band.

b) The x or y components, respectively, are over an order of magnitude smaller.

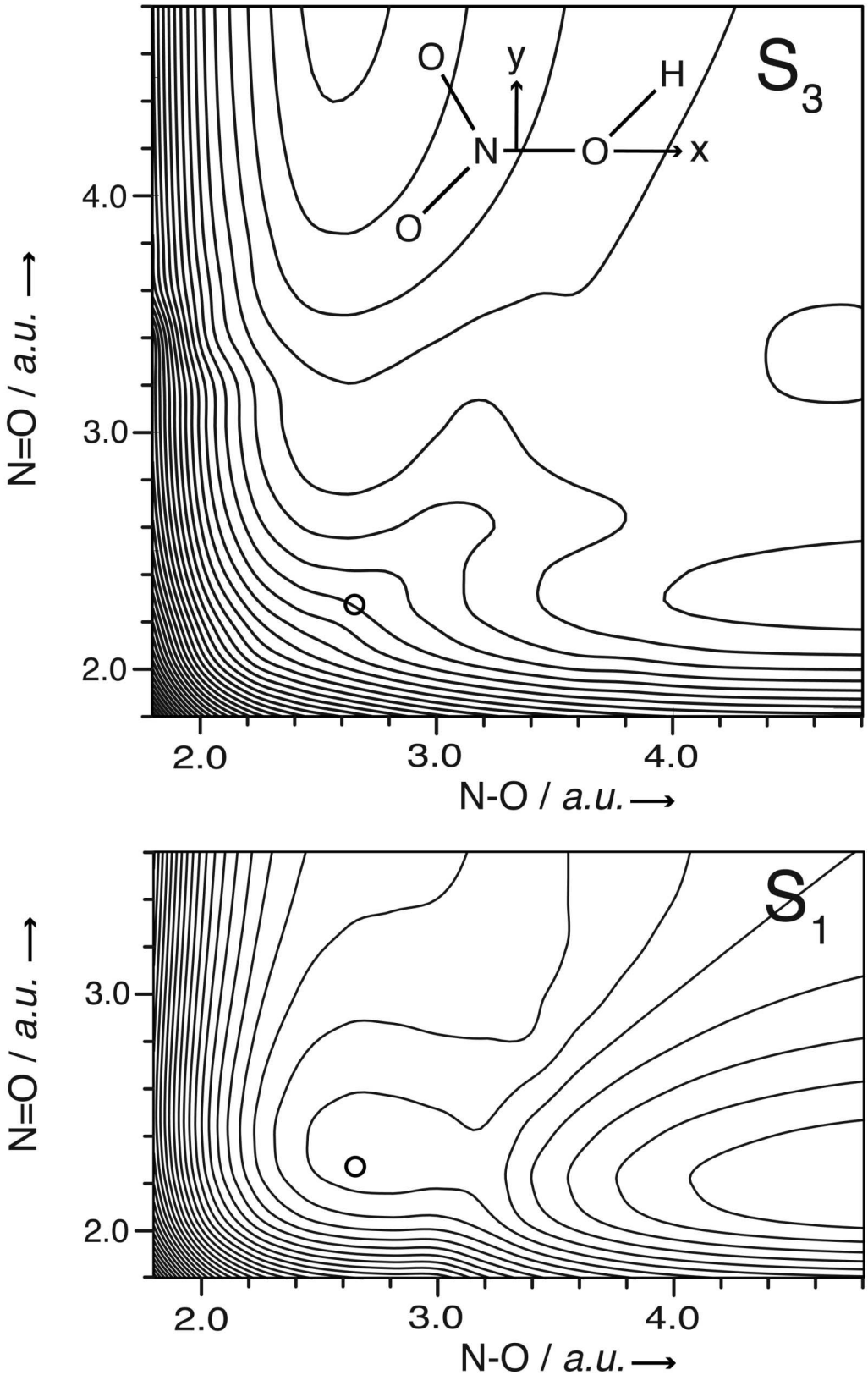


Figure 1

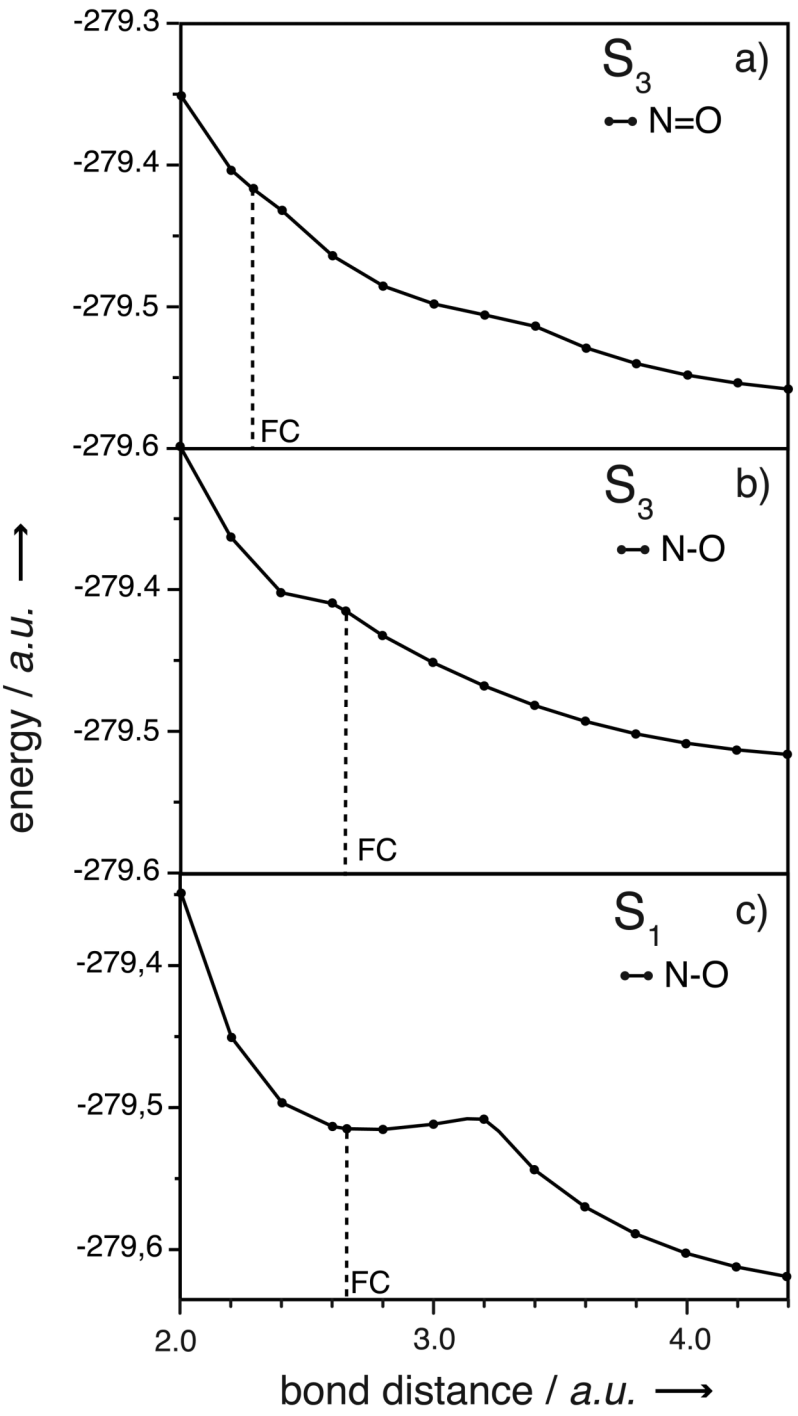

-279.3
-279.4
-279.5
-279.6
S3
a)
N=O
FC
S3
b)
N-O
FC
S1
c)
N-O
FC
-279,4
-279,5
-279,6
2.0
3.0
4.0
energy / a.u.
bond distance / a.u.

Figure 2

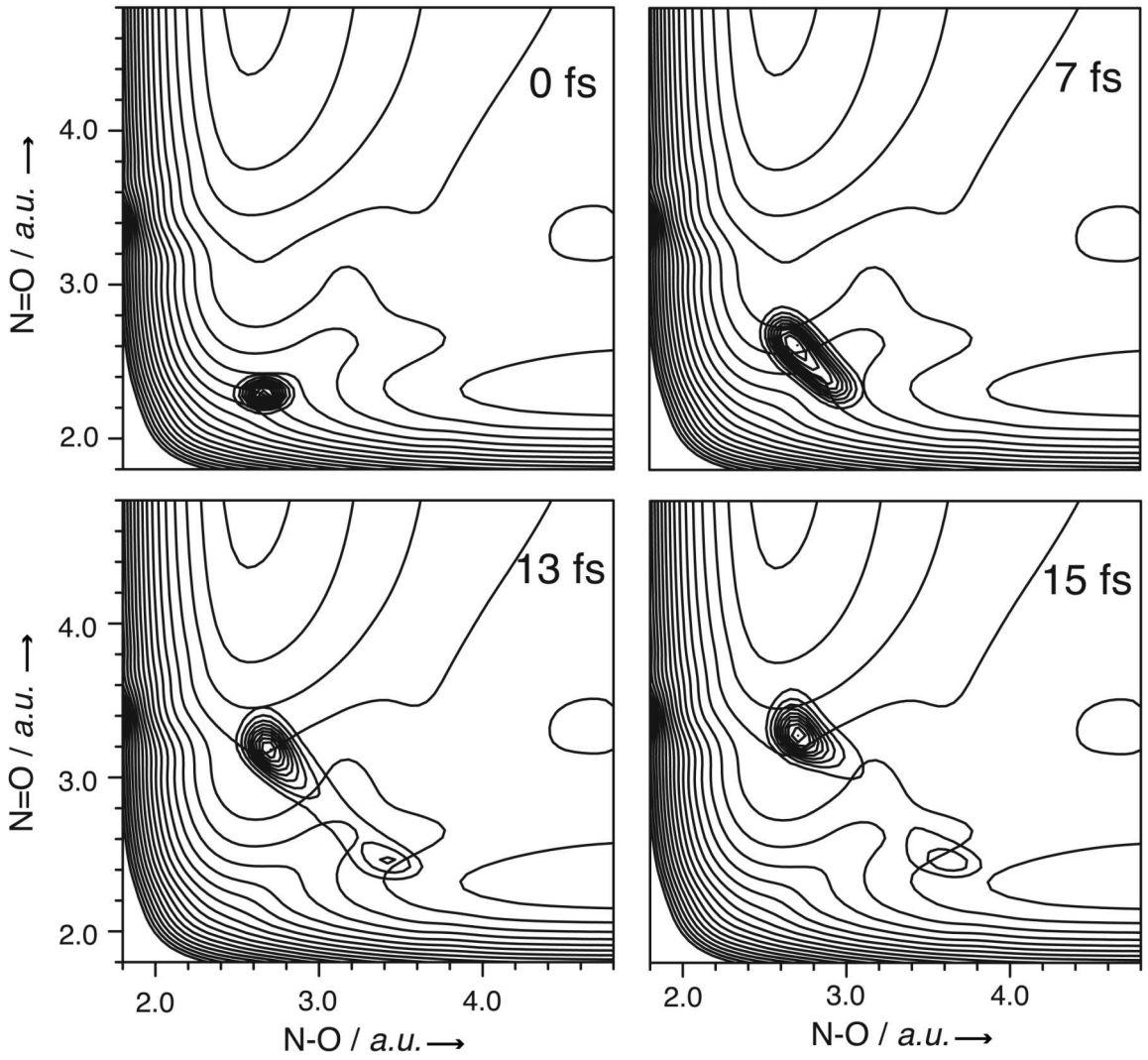
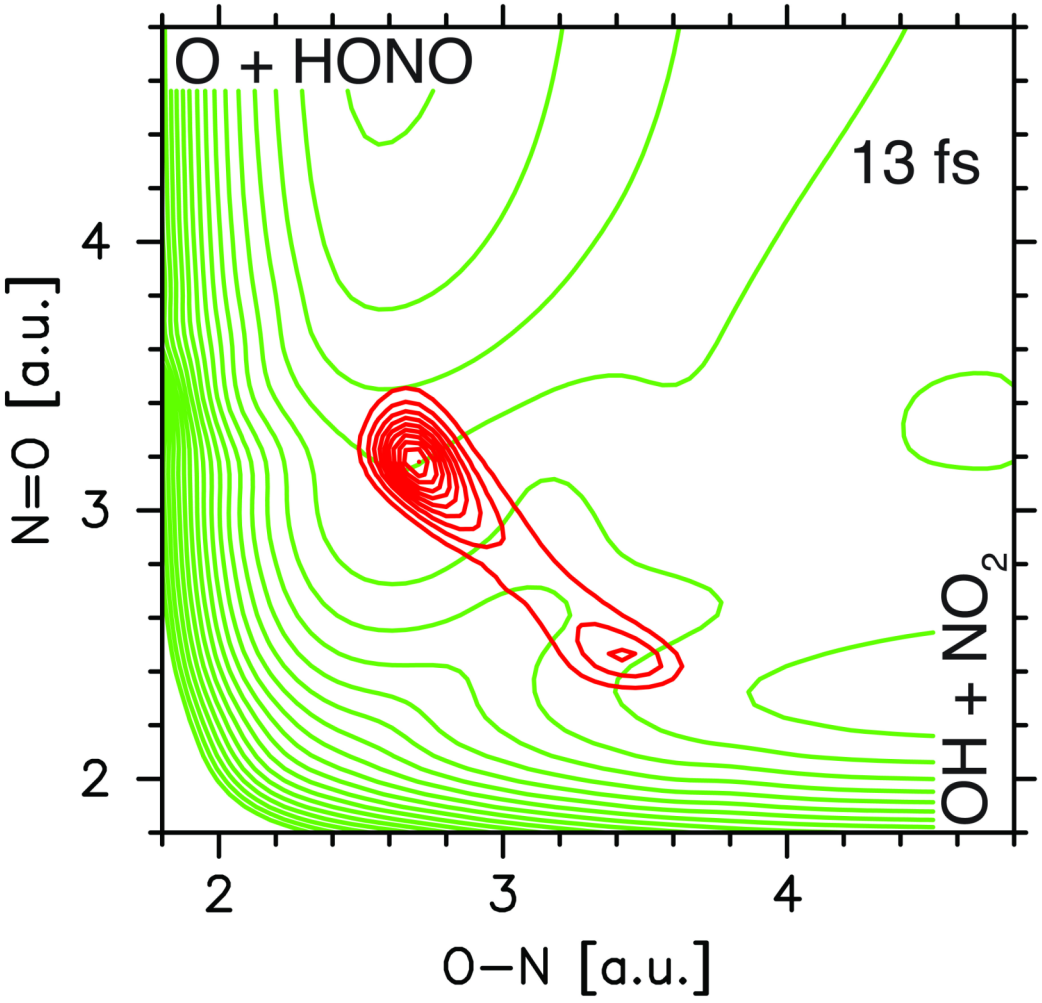


Figure 3



Graphical Abstract

The branching reaction in the S_3 state photodissociation of nitric acid HNO_3 visualized by a bifurcation of the wave packet after 13 fs of excitation.